behavior is exactly cancelled by the second term, which represents the image vortices. The final result for the interaction energy is

$$E_v = \frac{1}{4}\omega^2 \rho \pi R^4 = \frac{1}{2}I\omega^2, \qquad (69)$$

where I is the moment of inertia of a cylinder about its axis,  $I = \frac{1}{2}MR^2$ .

In general, vortices in an imperfect Bose gas exhibit properties similar to those of classical vortices. Here we have investigated the relation in detail for a vortex pair

PHYSICAL REVIEW

VOLUME 138, NUMBER 2A

of this work.

19 APRIL 1965

# Surface Tension of Liquid He4<sup>†</sup>

# K. R. ATKINS AND Y. NARAHARA\* Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania (Received 30 November 1964)

We have measured the surface tension of liquid He<sup>4</sup> down to 0.35°, using the capillary-rise method. The results are consistent with the theory that this temperature variation is mainly due to the excitation of surface modes similar to capillary waves. However, the results do not exclude an alternative theory, due to Singh, which considers the effect of the surface on the wave functions of an ideal degenerate Bose-Einstein gas. At the  $\lambda$  point, we observed a discontinuity (or at least a very rapid variation) of the first derivative with respect to temperature.

## 1. INTRODUCTION

HE surface tension of a liquid is a measure of the free energy associated with unit area of its surface. One of us has suggested<sup>1</sup> that, in the particular case of liquid helium, an important contribution to this surface free energy comes from surface modes of vibration. An exact quantum-mechanical treatment of these surface modes would be difficult, but a simple approach is to assume that they are similar to macroscopic capillary waves which have a frequency-dependent velocity given by the equation

$$c = (2\pi\sigma\nu/\rho)^{1/3},$$
 (1)

where  $\sigma$  is the surface tension,  $\rho$  the density of the liquid, and  $\nu$  the frequency of the wave. The assumption that Eq. (1) describes surface modes of all frequencies with a constant value of  $\sigma$  is analogous to the assumption in the Debye theory of the specific heats of solids that the modes of vibration of a solid lattice are sound waves and that there is no dispersion. As in the Debye theory, it is reasonable to assume that the highest frequency mode has a wavelength comparable with the average distance between neighboring atoms. This gives a cutoff frequency  $\nu_c \approx 1.5 \times 10^{11} \text{ sec}^{-1}$  and a characteristic temperature  $\theta_c = h \nu_c / k \approx 7^{\circ} \text{K}$ .

and for a system of many identical vortices. Experi-

mental studies<sup>2-4,29</sup> of liquid He II have been analyzed in terms of classical hydrodynamics; the present work

justifies such treatment as long as the distance between vortices is large compared to the dimension of the core.

**ACKNOWLEDGMENTS** 

discussion and criticism throughout the development

I should like to thank Professor P. C. Martin for

The zero-point energy of the surface modes is then found to represent about 60% of the total measured surface tension, emphasizing the importance of these modes. At temperatures small compared with the characteristic temperature  $(T \ll \theta_c)$ , the extra energy per unit area excited in the surface modes is

$$U = 2.07 \left(\rho/\sigma\right)^{2/3} h(k/h)^{7/3} T^{7/3}.$$
 (2)

The corresponding free energy is

$$U - TS = -\frac{3}{4}U$$
(3)

$$= -1.55 (\rho/\sigma)^{2/3} h(k/h)^{7/3} T^{7/3}.$$
 (4)

Assuming that this is the only factor influencing the variation of surface tension with temperature, the surface tension  $\sigma$  at a temperature  $T(\ll \theta_c)$  is related to the surface tension  $\sigma_0$  at 0°K by

$$\sigma = \sigma_0 - 1.55 \left( \rho / \sigma_0 \right)^{2/3} h(k/h)^{7/3} T^{7/3}. \tag{5}$$

Equation (5) is in approximate agreement with previous measurements of the surface tension.<sup>2-4</sup> However, all these measurements were made above 1°K and cannot be unambiguously extrapolated to 0°K to obtain

<sup>†</sup> Supported by grants from the National Science Foundation and the Research Corporation. This report is based on a thesis submitted to the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>\*</sup> Present address: Institute for the Study of Metals, University of Chicago, Chicago, Illinois.

<sup>&</sup>lt;sup>1</sup> K. R. Atkins, Can. J. Phys. 31, 1165 (1953).

<sup>&</sup>lt;sup>2</sup> A. T. van Urk, W. H. Keesom, and H. Kamerlingh Onnes, Proc. Roy. Akad. (Amsterdam) 28, 58 (1925). <sup>3</sup> J. F. Allen and A. D. Misener, Proc. Cambridge Phil. Soc. 34, 299 (1938). <sup>4</sup> K. N. Zinoveva, Zh. Eksperim. i Teor. Fiz. 29, 899 (1955) [English transl.: Soviet Phys.—JETP 2, 774 (1956)].

a good value of  $\sigma_0$ . Moreover, temperatures above 1°K are not sufficiently small compared with  $\theta_c \approx 7^{\circ}$ K). This is not merely a question of the mathematical approximations leading to Eq. (2). It is unreasonable to expect that a surface mode obeys Eq. (1) unless its wavelength is very much greater than the average interatomic distance. At  $T^{\circ}$ K, most of the excited modes have frequencies in the vicinity of kT/h. At 1°K, this is  $2 \times 10^{10}$  sec<sup>-1</sup>, which, according to Eq. (1), corresponds to a wavelength of  $3.3 \times 10^{-7}$  cm, only about 9 times the average interatomic distance. At 2°K, the corresponding wavelength is only about 6 times the average interatomic spacing.

An alternative theory has been proposed by Singh.<sup>5</sup> He considers the effect of the surface on the wave functions of an ideal degenerate Bose-Einstein gas and deduces that

$$\sigma = \sigma_0 - \frac{\pi m k^2 T^2 \xi(2)}{2h^2} \tag{6}$$

or

$$\sigma = \sigma_0 - 0.0075T^2. \tag{7}$$

Here *m* is the mass of a helium atom and  $\xi(2)$  is  $\frac{1}{6}\pi^2$ . Singh's formula is also in approximate agreement with previous measurements.

In an attempt to obtain further information on these issues, we have made extensive measurements of the surface tension down to  $0.35^{\circ}$ K.

#### 2. EXPERIMENTAL DETAILS

The surface tension measurements were made by the conventional capillary-rise method. The low temperatures were produced by a He<sup>3</sup> cryostat, but its design was influenced by the need to view the glass capillaries inside it. Figure 1 shows the important part of this cryostat. The experimental space is inside the glass



<sup>5</sup> A. D. Singh, Phys. Rev. 125, 802 (1962).

tube A connected to the brass end-plates B by indium O-ring seals. Liquid He<sup>4</sup> is introduced into this space through the stainless-steel capillary C. The copper evaporator E contains a small amount of liquid He<sup>3</sup>, which is reduced to a low temperature by pumping through the tube D. The glass capillaries F used for the surface-tension measurements are surrounded by copper shields G with viewing slits in appropriate places. Leads for a heater and a carbon-resistance thermometer are introduced through the Kovar terminals H. The whole of this experimental chamber is in a vacuum inside a second glass tube, which in its turn is immersed in the main liquid-helium bath. Heat radiation through the unsilvered strips of the Dewars introduced about 600 erg/sec to the experimental chamber. These unsilvered strips were therefore shielded leaving only small viewing windows adjacent to the capillaries, and the heat influx was thereby reduced to 150 erg/sec.

Since the liquid meniscus inside the experimental space was ill defined, we compared the heights of the menisci in two glass capillaries of different radii. The radius of a capillary was determined by filling it with mercury and measuring the length and mass of the mercury column. This was performed several times on each capillary and the results were found to be reproducible to about 0.5%. As a further check, some of the capillaries were cut at a point near where the liquidhelium meniscus was located in the capillary-rise measurements and Polaroid pictures of the cross section were taken with the aid of a projection microscope. This gave results within 1% of the mercury-column method. Several different pairs of capillaries were used. The smaller capillaries had inner radii in the range between 0.007 and 0.014 cm and wall thicknesses of about 0.001 cm. The larger capillaries had inner radii in the range between 0.024 and 0.046 cm and wall thicknesses of about 0.01 cm. The difference in the heights of the two menisci was therefore about 0.5 cm.

The menisci were illuminated by a neon lamp turned down to the minimum brightness consistent with comfortable viewing. Heat-absorbing glass was inserted between the lamp and the cryostat. However, removing the heat-absorbing glass and turning up the brightness of the lamp produced no detectable change in the positions of the menisci. The menisci were viewed through a telemicroscope mounted on a micrometer slide. To check optical distortion by the six layers of glass between the capillary and the telemicroscope, we placed a scale in the position normally occupied by the capillaries and compared it with the scale on the micrometer slide. Without the glass vessels the standard deviation of a scale reading was  $7 \times 10^{-4}$  cm. With all the glass vessels in place and filled with liquid nitrogen or liquid helium, the standard deviation increased to  $9 \times 10^{-4}$  cm. This is about 4% of the change in height of the menisci over the temperature range between 0.35 and 1.4°K.

The temperature was measured by a  $\frac{1}{4}$ -W Allen-

Bradley carbon resistor with a resistance of 10  $\Omega$  at room temperature. It was installed as near to the glass capillaries as possible. It was calibrated against the vapor pressure of the liquid He<sup>3</sup> when the evaporator E was closed off and the experimental space was slowly warming up. We estimate that the maximum error introduced by this procedure was 0.01°K.

A more detailed description of the apparatus and procedure is contained in the Ph.D. thesis of Narahara.<sup>6</sup>

### 3. EXPERIMENTAL DIFFICULTIES

In the course of our investigation, we made more than 3000 separate measurements of the surface tension. Most of these were made in the He<sup>3</sup> cryostat already described, but some early measurements utilized a booster cryostat,<sup>7</sup> which produced temperatures down to 0.8°K. Several different capillaries were used. In Fig. 2, our measurements above 1°K are compared with those of previous workers.<sup>3,4,8</sup> It will be noticed that our



FIG. 2. Comparison of our measurements of surface tension above  $1^{\circ}$ K with those of previous workers.  $\odot$  Allen and Misener (Ref. 3); + Zinoveva (Refs. 4,8);  $\triangle$ , run with booster cryostat; •,  $\bigcirc$ ,  $\Box$ , different runs with He<sup>3</sup> cryostat.

values are consistently higher and that the discrepancy at  $1^{\circ}$ K is as much as 7%. We can offer no explanation of this, but, in view of the variety of circumstances under which our measurements were made, we would be surprised if they always had the same consistent error.

Our measurements did show a random variation from day to day. This took the form of a bodily upward or downward displacement of the surface-tension-versustemperature curve without change of shape. The magnitude of this displacement was  $\pm 0.7\%$ . We suspect that it was a consequence of variations in the capillary diameter due to thin layers of ice, solid air or other contaminants (the glass capillaries were washed in hot chromic acid and distilled water, but this procedure may



not have been adequate). Such layers need have been only about  $10^{-4}$  cm thick to explain the observed variations. Since we were primarily interested in the shape of the curves, we applied to them normalizing factors ranging from 0.993 to 1.005 until they all lay on top of one another.

In order to satisfy the third law of thermodynamics, the surface-tension-versus-temperature curve must have zero slope at 0°K. In most runs, it did level off at low temperatures in a well-behaved fashion. Sometimes, however, it showed a tendency to continue to rise with a finite slope, giving excessively high values of the surface tension below 0.7°K (Fig. 3). This was very probably caused by a small amount of radiant heat absorbed inside the capillary, producing a small temperature difference between the inside and the outside and a consequent small rise of the inner level due to the thermomechanical effect. The temperature difference would have been just large enough to enable the heat to leak out by evaporation, conduction down the liquid column, and conduction through the glass walls. All of these mechanisms become less efficient at lower temperatures, and so the temperature difference and its accompanying level difference would have become increasingly larger as the temperature was lowered. Calculation shows that the observed excess rise of about  $5 \times 10^{-3}$  cm corresponds to a temperature difference of about  $2 \times 10^{-3}$ °K, which could easily have been produced by a heat input of a few ergs per sec. (The total heat input to the experimental space was 150 erg/sec.) This point of view was supported by the fact that the anomalous rise could be simulated by placing a heater in the vapor phase near the capillaries. We have rejected all data for which the anomalous rise was obviously present. Also, once the effect was understood, we added extra shielding around the capillaries. However, we cannot be certain that a small residual thermomechanical effect is not present in all our data.

We also gave careful consideration to the possible disturbing influence of a small amount of He<sup>3</sup>. If, as a result of heat flush,<sup>9</sup> He<sup>3</sup> had collected in the vicinity of the meniscus, the measured surface tension would

<sup>&</sup>lt;sup>6</sup> Y. Narahara, Ph.D. thesis, University of Pennsylvania, 1963 (unpublished).

<sup>&</sup>lt;sup>7</sup>K. R. Atkins, M. H. Edwards, and G. T. Pullan, Rev. Sci. Instr. 26, 49 (1955).

<sup>&</sup>lt;sup>8</sup> We are grateful to Dr. Zinoveva for sending us some unpublished details of her measurements.

<sup>&</sup>lt;sup>9</sup> C. T. Lane, H. A. Fairbank, L. T. Aldrich, and A. O. Nier, Phys. Rev. 73, 256 (1948).



a 0.05% He<sup>3</sup>-He<sup>4</sup> mixture.

have been that of a He<sup>3</sup>-He<sup>4</sup> mixture. Alternatively, a difference in He<sup>3</sup> concentration between the inside and outside of the capillary would have led to an osmotic pressure, which would have influenced the level of the inner meniscus. We therefore filled our experimental space with a 0.05% He<sup>3</sup>-He<sup>4</sup> mixture and obtained the striking result shown in Fig. 4. The sharp dip below  $0.6^{\circ}$ K is probably due to one of the two effects mentioned above. This dip was never observed with the almost pure He<sup>4</sup>, containing about one part in  $10^{7}$  of He<sup>3</sup>, used in the main body of this research. The main problem was the anomalous *rise* already discussed above.

# 4. COMPARISON WITH THEORY

After rejecting the data which showed an obvious anomalous rise below 0.7°K, we still had about 3300



FIG. 5. A comparison between the experimental data and the theoretical curve given by Eq. (5).

separate measurements of surface tension, most of which were in the range from 0.35 to 1.4°K. We divided this temperature range into intervals of 0.01°K and averaged all the data in each interval. This averaged data was used to plot Figs. 5, 6, and 7, and in the curve-fitting computations. Figure 5 compares the data with Eq. (5). In this equation the only adjustable parameter is  $\sigma_0$ and, if the value  $0.3718 \text{ erg/cm}^2$  is adopted for this parameter, one gets the best fit to the experimental data, using the method of least squares. It will be seen that the fit is only approximate, since the experimental data lie entirely above the curve below 0.8°K and entirely below the curve above 1.0°K. This suggests three possibilities. First, there may still be a thermomechanical effect increasing the data below 0.7°K. Second, the temperature range may not be low enough to ensure that all the excited surface modes obey Eq.



FIG. 6. An attempt to fit the experimental data to the equation  $\sigma = \sigma_0 - AT^n$ . The arrows show the extent of scatter of the original data before averaging.

(1). Third, the variation of surface tension with temperature may be partially due to factors other than the surface modes.

We also used the method of least squares to fit an equation of the form

$$\sigma = \sigma_0 - A T^n, \qquad (8)$$

with  $\sigma_0$ , A, and n all considered to be variable parameters. The best fit was obtained with  $\sigma_0 = 0.3729$ , A = 0.0081, and  $n = 2.5 \pm 0.2$ . In Fig. 6 the experimental data is compared with the empirical curve

$$\sigma = 0.3729 - 0.0081 \ T^{2.5}. \tag{9}$$

The agreement is now much better. The value of  $2.5\pm0.2$  for the power of T is consistent with the value 2.33 suggested by Eq. (5). However, if the value of A were calculated by putting  $\sigma_0=0.3729$  into Eq. (6), it

would be 0.0066 as compared with the value of 0.0081 used in Fig. 6 to obtain the best fit.

Equation (7), due to Singh,<sup>5</sup> gives values of  $(\sigma_0 - \sigma)$  which differ from the experimental data by as much as 20%. However, as shown in Fig. 7, the data can be represented reasonably well by the equation

$$\sigma = 0.3745 - 0.0096 T^2. \tag{10}$$

Singh's theory applies to an ideal gas and it is not clear how it should be modified to include atomic interactions. Therefore, it cannot be said that our data



FIG. 7. An attempt to fit the experimental data to the equation  $\sigma = \sigma_0 - AT^2$ .

exclude the possibility that Singh's approach is correct in principle.

We conclude that our measurements are in approximate agreement with both theories, but there are significant deviations. There remains a need both for refinement of the theories and further measurements of the surface tension, perhaps by an entirely different method.

#### 5. THE $\lambda$ TRANSITION

We have also made a careful study of the behavior of the surface tension in the vicinity of the  $\lambda$  point, using



FIG. 8. The surface tension in the vicinity of the  $\lambda$  point.

the apparatus of Fig. 1. With exchange gas in the space surrounding it, the experimental chamber was brought to the same temperature as the main bath, which was in the vicinity of 2°K. The exchange gas was then removed and the temperature of the experimental space was made to rise slowly through the  $\lambda$  point by supplying a steady amount of heat to a heater immersed in the He<sup>4</sup>. Meanwhile the main bath was kept at a constant temperature by an electronic regulator.<sup>10</sup> The temperature of the liquid He<sup>4</sup> in the vicinity of the capillaries was measured by a carbon resistor. To calculate the surface tension from the measurements of the heights of the menisci, we use the values of liquid density near the  $\lambda$  point obtained by Edwards<sup>11</sup> and Kerr.<sup>12</sup> Figure 8 shows the results of a typical run. Careful inspection of the points reveals that there is no evidence for a discontinuity in  $\sigma$  at the  $\lambda$  point, but that there does appear to be a discontinuity in the slope  $d\sigma/dT$ . At the very least, it can be said that  $d\sigma/dT$  is a rapidly varying function of temperature in the immediate vicinity of the  $\lambda$  point. If straight lines

$$\sigma = \sigma_{\lambda} - \alpha (T - T_{\lambda}) \tag{11}$$

are fitted separately to the points above and below the  $\lambda$  point, there is a significant difference in their slopes. Below the  $\lambda$ -point  $\alpha_{II}=0.093\pm0.005$ . Above the  $\lambda$  point,  $\alpha_{I}=0.074\pm0.005$ .

<sup>12</sup> E. C. Kerr (private communication).

<sup>&</sup>lt;sup>10</sup> H. S. Sommers, Rev. Sci. Instr. 25, 793 (1954).

<sup>&</sup>lt;sup>11</sup> M. H. Edwards, Can. J. Phys. 36, 884 (1958).